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IRON OXIDE AS AN EFFECTIVE CATALYST FOR THE POLYCONDENSATION OF BENZYL CHLORIDE. THE FORMATION OF PARA-SUBSTITUTED POLYBENZYL

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Iron oxides prepared by calcining iron hydroxides which were precipitated by hydrolyzing $FeCl_3$ and $Fe(NO_3)_3$ with ammonia and iron nitrate at 300-500°C were highly effective for the title reaction at room temperature. The product was stable up to 400°C and predominantly para-substituted polybenzyl with 8175 of molecular weight.

Polycondensation of benzyl chloride with simultaneous evolution of hydrogen chloride has generally been carried out with Lewis acid catalysts such as $SnCl_4$ 1,2,3) and $AlCl_3$.4) The linear para-substituted polybenzyl formed by this reaction is known to be one of the thermally stable polymers.5) In a previous paper,6) it was reported that calcined iron sulfate, especially the sulfate calcined at 700°C, was exceedingly active for this polymerization. The product was shown to consist of predominantly para-substituted structure with 3550 of molecular weight. We now wish to report that the prepared iron oxides are surprisingly active for the reaction to form the same type of polymer with molecular weight more than 8000.

$Fe(OH)_3$-I and -II were precipitated by hydrolyzing $FeCl_3$ and $Fe(NO_3)_3 \cdot 9H_2O$, respectively, with aqueous ammonium hydroxide. They were washed and then dried at 100°C. $Fe(NO_3)_3$ was prepared by heating $Fe(NO_3)_3 \cdot 9H_2O$ (Wako Pure Chemical Co.) at 150°C for 2-3 h. The dried catalysts were powdered below 100 mesh, calcined in Pyrex glass tubes in air for 3 h and stored in glass ampoules until use. Benzyl chloride (guaranteed reagent of Wako Pure Chemical Co.) were used without further purification. Polymerization was carried out at room temperature without solvent, together with the weighed catalyst. When 0.1 g of iron oxide prepared

Table 1. Catalytic Activity of Iron Oxide for the Bulk Polymerization of Benzyl Chloride at Room Temperature[a)]

Run	Catalyst	Temp. of calcn. (°C)	Reaction time (s)	Yield[b)] (%)	[η][c)]
1	$Fe(OH)_3$-I	300	7	56	0.111
2		400	15	67	
3		500	28	70	
4		600	53	69	
5		700	9.3 min	69	
6	$Fe(OH)_3$-II	300	10	55	0.115
7		400	27	68	
8		500	25	69	
9		600	17.2 min	71	
10	$Fe(NO_3)_3$	300	32	69	0.121
11		400	28	71	
12		500	68	64	

a) 5 ml of benzyl chloride and 0.11-0.13 g of catalyst were used of each reaction.

b) Methanol-insoluble portion.

c) Intrinsic viscosity. Determined by 0.25-1.0 g of polymer in 100 ml of benzene at 25°C.

by calcining $Fe(OH)_3$-I or -II at 300°C was added to 5 ml of benzyl chloride at room temperature, polymerization occurred immediately with violent evolution of HCl. The reaction was almost explosively complete in less than 10 sec to give a brownish, dry and foamy solid. After the reaction, the polymer was dissolved in benzene, separated from the catalyst by filtration, washed with water, dried and finally poured into excess methanol. The precipitated polymer was collected, washed with methanol and dried in vacuum. Viscosity was determined in benzene at 25°C in a Cannon-Fenske viscometer.

Table 1 shows activities of catalysts, together with yields and viscosities of the product. The iron oxides prepared by iron hydroxides and nitrate at 300-500°C were exceedingly active for the polymerization; the $Fe(OH)_3$-I catalyst

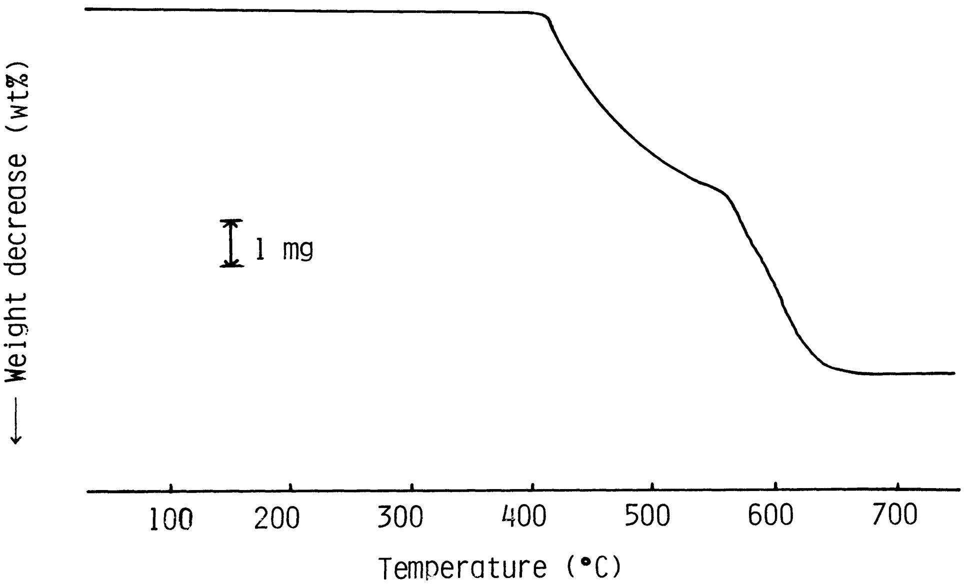

Fig. 1. TG curve of the polymer produced by $Fe(OH)_3$-I calcined at 300°C (Run 1). Sample: 8 mg. Heating rate: 10°C/min.

heat-treated at 300°C appears to be the most active. The product of each reaction in the Table was quite similar in appearance, yellowish white powder after purification. The catalysts prepared by calcining Fe_2O_3 (Wako Pure Chemical Co.) at 200 and 400°C were inactive at all even over a period of 48 h. DTA of $Fe(OH)_3$-I, -II and $Fe(NO_3)_3$ showed that these materials crystallize at 410-430°C, but the Fe_2O_3 did not show any crystallizing temperature up to 700°C on DTA. Thus, the crystal structure of the present iron oxides seems to differ from that of the commercial one.

The physical and chemical properties of the polymers given by the catalysts of $Fe(OH)_3$-I and -II and $Fe(NO_3)_3$ calcined at 300°C (Run 1, 6 and 10 in the Table) were examined. The intrinsic viscosity was $[\eta] = 0.111-0.121$. Elemental analysis showed 6.66-6.76 % for H and 93.04 - 93.52 % for C; this indicates that chlorine contained in the product is negligible. NMR spectroscopy showed two broad singlets [δ 6.94 (4H, phenylene H) and 3.7 ppm (2H, CH_2)] for the three materials. From the elemental and NMR analyses it is indicated that the product is predominantly linear para-substituted polybenzyl.

The TG analyses in air of the three samples were exactly coincident, and one of them is shown in Fig. 1. The polymer is thermally stable up to 400°C above which decomposition occurs. The polymer decomposed 50 % at 550°C and 100 % at 660°C.

The molecular weight of the sample in Run 1, which was measured in benzene at 37°C by vapor pressure osmometry, was determined to be 8175. Thus the degree of polymerization is ca. 90. It has been reported that the product has molecular weight less than 1200 and a branched polymer in the case of reactions using Lewis acid catalysts.[1-4]

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